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(Article begins on next page)

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Bioaccessibility and size distribution of metals in road dust and roadside soils along a peri-urban transect.

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Abstract

Road dust (RD), together with surface soils, is recognized as one of the main sinks of pollutants in urban environments. Over the last years, many studies have focused on total and bioaccessible concentrations while few have assessed the bioaccessibility of size-fractionated elements in RD. Therefore, the distribution and bioaccessibility of Fe, Mn, Cd, Cr, Cu, Ni, Pb, Sb and Zn in size fractions of RD and roadside soils (<2.5 µm, 2.5-10 µm and 10-200 µm) have been studied using aqua regia extraction and the Simple Bioaccessibility Extraction Test.

Concentrations of metals in soils are higher than legislative limits for Cu, Cr, Ni, Pb and Zn. Fine fractions appear enriched in Fe, Mn, Cu, Pb, Sb and Zn, and 2.5-10 µm particles are the most enriched. In RD, Cu, Pb, Sb and Zn derive primarily from non-exhaust sources, while Zn is found in greater concentrations in the <2.5 µm fraction, where it most likely has an industrial origin.

Elemental distribution across soils is dependent on land use, with Zn, Ni, Cu and Pb being present in higher concentrations at traffic sites. In addition, Fe, Ni and Cr feature greater bioaccessibility in the two finer fractions, while anthropic metals (Cu, Pb, Sb and Zn) do not.

In RD, only Zn has significantly higher bioaccessibility at traffic sites compared to background, and the finest particles are always the most bioaccessible; more than 90% of Pb, Zn and Cu is bioaccessible in the <2.5 µm fraction, while for Mn, Ni, Sb, Fe and Cr, values vary from 76% to 5%. In the 2.5-10 µm fraction, the values were 89% for Pb, 67% for Zn and 60% for Cu.

These results make the evaluation of the bioaccessibility of size-fractionated particles appear to be a necessity for correct estimation of risk in urban areas.

Keywords

SBET, bioavailability, brake wear, heavy metals, PM10, non-exhaust

1. Introduction

In Europe, urban areas host three-quarters of the population. However, urbanization is still ongoing and, nowadays, peri-urban spaces are increasing at a much faster rate than traditional core cities (European Commission, 2011). One of the consequences of the expansion of urban areas on the environment is soil and air pollution. This is currently one of the primary causes of concern for human health (Lim et al., 2012).

Road dust (RD) is at the interface between the soil and atmosphere, being a complex environmental medium originating from both natural and anthropogenic processes. Major sources include particles from soil materials, vehicle exhaust and non-exhaust emissions, atmospheric deposition and industrial activities (Thorpe and Harrison, 2008; Pant and Harrison, 2013). Together with surface soils, RD is a source and a sink of various pollutants in urban environments (Biasioli et al., 2006; Christoforidis and Stamatis, 2009). Metals are one of the most problematic as they are potentially toxic, persistent in the environment and often present at high concentrations.

RD and soil particles can be easily re-suspended by vehicles or wind, resulting in an important source of atmospheric particulate matter (PM) (Amato et al., 2009; Pant and Harrison, 2013). In recent years, research has focused on RD characterization and source apportionment of mineral PM (Aimar et al., 2012; Fujiwara et al., 2011; Kumar et al., 2013; Putaud et al., 2010). Concerns over RD contributions are growing based on the lack of legislation pertaining to all non-exhaust sources (Amato et al., 2014; Kousoulidou et al., 2008; Querol et al., 2004). In fact, with the continuous reduction of exhaust emissions, non-exhaust particles will increase their contribution to the total vehicle-generated particulate matter and may become dominant over the coming years in terms of both emissions and contributions to air quality (Denier van der Gon et al., 2013).

In city environments, metals in soil and RD can exert their toxicity through entering the human body via inhalation, dermal contact and ingestion, with ingestion being the most likely pathway for RD and soil fine particles (for example, $<50\ \mu\text{m}$) (Siciliano et al., 2009; Ruby and Lowney, 2012). Shi et al. (2011) calculated that, for children, ingestion contributed 97.5% and 81.7% to total exposure doses of non-carcinogenic and carcinogenic elements, and that the contribution rates for adult were 91.7% and 52.9%, respectively. Kong et al. (2012) computed that for $<2.5\ \mu\text{m}$ and $<10\ \mu\text{m}$ particles of RD, non-carcinogenic risks based on exposure to metals were two orders of magnitude higher for ingestion than for inhalation.

While a number of studies on RD have concentrated on the elemental composition of samples (Amato et al., 2011; Gunawardana et al., 2012; McKenzie et al., 2008; Varrica et al., 2003), few have considered that the total or pseudo-total content does not necessarily represent the most dangerous chemical fraction of the metal. Analogously, whole soil content would not serve as a reliable assessment of the transfer potential of particles, as the coarser fractions are rarely removed (Bi et al., 2015; Paustenbach, 2000; Turner and Ip, 2007). Therefore, an evaluation of metal bioaccessibility is necessary to better evaluate human health risks owing to metals in order to obtain a more realistic ingestion exposure (Hu et al., 2011; Yu et al., 2014).

As there is a general need to better define the hazards and the health relevance of RD and non-exhaust PM sources (Denier van der Gon et al., 2013; Guney and Zagury, 2016), the aim of this study was to assess the total and bioaccessible concentrations of metals in size-resolved fractions of RD and roadside soils in Turin (Italy).

2. Experimental

2.1 Study area

The metropolitan area of Turin (Italy) ($45^{\circ}04'\ \text{N}$; $7^{\circ}41'\ \text{E}$) has a population of 1.7 million inhabitants and is the fourth most populated metropolitan area in Italy. It is characterized by a very high volume of vehicular traffic and has a long industrial history, mainly because of the automotive and metallurgical industries. The city was built and extended at the bottom of an alluvial plain in the Po valley, and is shielded by hills to the

east and by the Alps to the north and west. This setting causes PM levels to often exceed EU limits not only in Turin, but also in many other urban areas within the Po valley (Eeftens et al., 2012; Padoan et al., 2016), and these atmospheric emissions can result in a major source of diffuse metal soil contamination (Biasioli and Ajmone Marsan, 2007).

10 sampling sites were selected along a peri-urban transect (7.5 km), starting near the ring road and reaching the city center along an approximately straight line (Figure 1). Six sites were on a main road (Corso Allamano) and can be separated into three groups: samples influenced by industrial activities (A1, A2), sites located in a residential area (S1, S2) and sites surrounded by agricultural fields (A3, A4). In addition, each group included a sampling spot just before a traffic light or a roundabout (braking sites: A1, A4, S1) and one at least 200 m after (acceleration sites: A2, A3, S2). All sites have a similar traffic intensity, varying between 13000 (S1, S2) and 9500 (A3, A4) vehicles day⁻¹ (data provided by 5T s.r.l.). The industrial area and the residential area counted with one additional sampling site each, located on a secondary road, with a mean traffic of 1000 and 3000 vehicles day⁻¹, respectively, to appreciate the impact of low traffic volumes. Two urban background sites were additionally sampled - a paved road within the largest park of the city (PE) and within the university campus (AG), as remotely as possible from direct traffic sources but still in the urban area. Soil samples were collected as close as possible to the RD sampling point.

At each site, samples were gathered during three different seasons: April 2015, August 2015 and February 2016, after, at least, seven dry days. In order to minimize time variability between sampling sites, during each season, all samples were collected on the same day.

2.2 Sampling methodology

At each site, three subsamples of RD were collected, 1 m² each, centered within the right-most active lane using a polyethylene brush (Acosta et al., 2011; Li et al., 2013; Sutherland et al., 2012; Varrica et al., 2003). This method could result in a loss of fine particles, so special care was taken to avoid re-suspension during the sampling by sweeping directly into a plastic bag. The collected sample quantities varied from 20 to 200 g.

Soil samples were taken from a 0–5 cm depth at all locations and within 2 m from the edge of the road. At each site, three sub-samples were collected at a distance of 1 m between each other, and the sub-samples were homogenized into one composite sample for further analysis. The brush and shovel were been washed with a mild acidic solution and deionized water before and between samplings. All samples were air dried in the laboratory at room temperature and passed through a plastic 2-mm sieve prior to laboratory analyses.

2.3 Analytical procedures

All samples were analyzed for pH (1:2.5, soil:water), total carbon (TC) and nitrogen (TN) (CE Instruments, NA2100 Elemental Analyzer, ISO 10694) and carbonates (volumetric method, ISO 10693). The particle-size distribution (PSD) was measured via the hydrometer method (Colombo and Miano, 2015; Gee and Bauder, 1986).

RD and soil samples were partitioned into four size fractions (<2.5, 2.5-10, 10-200 and 200-2000 µm). Samples were dispersed with Na-hexametaphosphate and resuspended, with the <2.5 µm fraction separated by centrifugation (ALC-4227R) while the remaining fractions were separated by repeated sedimentation and decanting (Ajmone-Marsan et al., 2008); the process was repeated until the supernatant was clear. Following separation, the fractions were dried prior to analysis.

An *aqua regia* (HCl/HNO₃, 3:1 v/v) extraction was performed with microwave digestion of 0.5 g of sample (Milestone Ethos D, ISO 11466). Extractable (pseudo-total) content of Fe, Mn, Cd, Cr, Cu, Ni, Pb and Zn were determined in bulk samples (ground to pass through a 150-µm sieve prior to analysis) and in the <2.5-, 2.5-10-, 10-200-µm fractions by flame atomic absorption spectrometry (FAAS) (Perkin-Elmer AA-400), while Sb was detected by HG-AAS (Perkin-Elmer 4100 equipped with a FIAS 400 hydride generator). The coarse sand fraction (200-2000 µm) was not analyzed because it was determined to be outside the scope of this research, which focused on inhalable or ingested particles. Accuracy was verified using certified reference materials for

aqua regia-soluble contents (CRM 141R, Community Bureau of Reference, Geel, Belgium) and recovery is reported in Supplementary Material (Table SM1). All reagents were of an ultrapure or analytical grade.

Metal bioaccessibility was assessed using a widely employed and validated *in vitro* extraction method, the Simple Bioaccessibility Extraction (SBET) method (Oomen et al., 2002; Ruby et al., 1999). It was developed for soils and was recently utilized for the first studies on RD, albeit being performed without size fractionation (Bi et al., 2015; Li et al., 2014; Patinha et al., 2015; Turner and Ip, 2007). Half a gram of sample was mixed with 50 ml of a 0.4 M glycine solution with pH adjusted to 1.5 with concentrated HCl. Extraction was performed for 1 h at 37°C (USEPA Method 1340, 2013). The mixture was then centrifuged and the supernatant filtered through cellulose filter (Whatman N°4). The SBET extract metal concentrations were determined by FAAS and HG-AAS.

Detection (LOD) and quantification limits (LOQ) for the methods were calculated with the calibration curves. According to the ICH Harmonized Tripartite Guideline (ICH, 2005), the following equations were used:

$$\text{LOD} = 3.3 \sigma_a/S \quad \text{LOQ} = 10 \sigma_a/S$$

where σ_a represents the standard deviation of the intercept of regression line and S is the slope of the calibration curve. Recovery tests were carried out using blank solutions spiked with metals at three concentration levels (0.1 – 20 mg/kg) and using a previously well-characterized soil. Results for LOD, LOQ and recoveries are reported in the Supplementary Material (Table SM1). As no certified reference material was available for this method, results were considered satisfactory when the variation coefficient between duplicates was lower than 10%.

Enrichment factors (EF) of elements were calculated according to:

$$EF = \left(\frac{C_{Me}}{C_{Re}} \right)_{\text{Sample}} / \left(\frac{C_{Me}}{C_{Re}} \right)_{\text{Crust}}$$

where (C_{Me}/C_{Re}) is the concentration ratio between the metal and the reference element in the sample and in the earth's upper crust as reported by Wedepohl (1995). We also computed the EF_L , relative to the local background values in Turin soils, for Cr, Ni, Cu, Pb, Sb and Zn based on the ISO 19258/2005 norms from the Regional Agency for Environmental Protection (ARPA Piemonte, 2015). The natural background value was provided for Cr and Ni, while the natural-anthropogenic background for Pb, Cu, Zn and Sb. This last value originates from the sum of the concentrations based on natural and diffuse anthropic sources, such as atmospheric deposition and agronomic operations, and was calculated for the topsoil (0-10 cm). Statistical analysis, including analysis of variance (ANOVA), Student's t-test, Pearson correlations and hierarchical cluster analysis (HCA), was conducted by means of SPSS v.22 software (IBM Corporation, Armonk, NY).

3. Results and discussion

3.1 Physicochemical properties of soils

Table 1 lists the mean values of the measured soil and RD properties. The soils' average pH was slightly alkaline, which is in agreement with previous studies reporting that city soils have higher pH than the adjacent agricultural soils, probably for the historical inclusion of extraneous material, such as construction debris (Biasioli et al., 2006). For the same reason, soils have a high sand content (50 μm – 2 mm), with a mean of 70% (Biasioli et al., 2006). Particles <2.5 and 2.5-10 μm had mean concentrations of 8% and 6%, respectively.

TC content in roadside soils was high on the average, potentially reflecting the accumulation of plant residues, as these areas are rarely disturbed. However, part of this content may also be ascribable to anthropic organic contaminants derived from oils, gasoline, brake pads and organic compounds within asphalt.

Average metal content (*aqua regia* extraction) in the bulk samples is reported in Table 2, and is compared to a previous extensive study of city soils (Biasioli et al., 2006). In bulk soils, concentrations were high for all

metals considering that, according to the Italian legislation (MATTM, 2006), average values of Cu, Cr, Ni, Pb and Zn were above the limits for residential and green areas (120 mg/kg, 150 mg/kg, 120 mg/kg, 100 mg/kg and 150 mg/kg, respectively). The values observed in this study were also higher than reported in previous studies in Turin (Biasioli and Ajmone-Marsan, 2007), which included ornamental garden and park sites, highlighting the impact of traffic emissions. Comparing these findings with other industrial cities worldwide (Ajmone-Marsan and Biasioli, 2010), our results place Turin in the higher range for all metals. These metals can be released from different sources - Pb could mainly derive from historical leaded fuel and paints, Sb and Cu from brakes and Zn from tires (Grigoratos and Martini, 2015; Thorpe and Harrison, 2008 and references therein). Ni and Cr, conversely, naturally contribute in high proportions as they may derive from the alteration of serpentinite rocks present in the alluvial deposits upon which the soils developed, as described in previous studies (Ajmone-Marsan et al., 2008; ARPA Piemonte, 2015; Biasioli et al., 2006). Other sources can be heavy oil combustion, metallurgical industries, vehicle factories and traffic.

3.2 Physicochemical properties of RD

The average pH of RD samples was very close to that of soils, but with a higher variability probably related to a higher amount of carbonates. The separation of RD samples into particle sized fractions uncovered that RD was coarser than soils. Sand was still the dominant fraction, however, while fractions <2.5 μm and 2.5-10 μm ranged from 0.6 to 24 % and from 0.2 to 8 % sand. The C/N ratios were much higher than in roadside soils, indicating an addition of C from non-natural sources, such as organic contaminants and bitumen.

In RD samples, average elemental concentrations were comparable with previous studies in other cities of the world (Christoforidis and Stamatis, 2009; Hu et al., 2011; Acosta et al., 2011) except for Ni and Cr, having higher values in Turin, which is in line with their local geogenic origin. Most of the metals have average concentrations close to those of the soil samples, while only Mn and Pb had significantly lower means in RD (t-test: $p = 0.05$). However, comparing concentrations across the six sites ($n = 18$), where both soil and RD were sampled, only Fe was well correlated between the soil and RD samples ($r = 0.80$, $p < 0.01$), while other metals did not exhibit a significant correlation. This behavior was probably based on the different strengths of the anthropogenic sources of metals between sites, while RD Fe could have a main geogenic (soil) contribution.

3.3 Seasonal and spatial variability

Seasonality in soil and RD metal concentrations was evaluated by comparing mean values from different seasons at both traffic ($n = 8$) and background sites ($n = 2$). No seasonal variability was observed in soil samples at either site. With RD samples from traffic sites, Fe was significantly higher in concentration (t-test, $p < 0.05$) in the summer and spring than in the winter, potentially because of the lower soil resuspension in the latter season. At background sites (PE and AG), similar results were also found, with the highest values for Fe and Mn being in the summer, although they were not significant.

Average bulk concentrations of Fe, Mn, Cr, Ni, Cu, Pb, Sb and Zn at each site were reported in Figure 2.

In the soil samples, Fe, Mn, Ni and Cr had low spatial variability, and the average of the traffic sites was not statistically different from the background sites. On the contrary, Cu, Pb, Sb and Zn had significantly ($p < 0.05$) higher concentrations at traffic sites, with the highest being at the A2 and S1 sites, and the lowest at the two background sites (AG and PE). This indicated road traffic as the main source of these metals. Pb was found at the highest concentration among metals (and the highest EF), consistent with its remarkable use in various human activities, such as a gasoline fuel additive, that have contaminated roadside soils (Ajmone-Marsan and Biasioli, 2010).

In RD samples, the spatial variability of Fe, Mn, Ni and Cr is more pronounced, with higher concentrations at the A2 and RI sites located in an industrial area. As in the soils, average Fe content at traffic sites was not significantly different from background sites (although higher, 24.9 versus 20.2 g/kg). This, considering also the significant correlation between Fe in RD and soil samples, could indicate that a substantial proportion of

Fe was soil-derived. If so, the higher variability between the sites could be because of the different contribution of soil to RD.

Cu, Pb, Sb and Zn had similar spatial patterns, with higher concentrations at the A1 and A2 sites (the most trafficked) near the industrial zone, and at sites in the city center (S1, S2, BO). Conversely, the A3, A4 and RI sites, with lower traffic or located near agricultural areas, featured lower concentrations that were not statistically different from the background sites (AG, PE). Therefore, correlations between soil and RD concentrations at these last five sites were calculated ($n = 15$, A2 soil for RI site in view of their proximity), obtaining a significant correlation not only for Fe, but also for Cu and Pb ($p < 0.05$, $r = 0.84$, 0.90 and 0.72 , respectively). This suggests that at sites with low vehicular traffic, urban soils could be one of the major origins for these metals in RD.

In order to confirm these associations, Pearson correlations for RD samples were calculated ($n = 28$, $p = 0.05$), as reported in the Supplementary Material (Table SM2). TC and TN appeared strongly related, as are Fe and Mn along with Cr and Ni, suggesting a common origin from soil material. Cu, Sb, Pb and Zn were significantly correlated with each other, as well, confirming the hypothesis of a single source. In fact, Sb and Cu could have emanated from brake wear (Grigoratos and Martini, 2015), Cu and Pb from the resuspension of contaminated roadside soils and Zn could derive from tire wear (Harrison et al., 2012), validated by the significant, albeit low, correlation with TC. Cd is the only metal without any significant association with other metals, probably having a different anthropic (industrial) origin.

3.4 EFs

EFs of the elements in soils and RD relative to upper crustal composition (Wedepohl, 1995) and to the local soil composition are reported in the Supplementary Material (Tables SM4 and SM5). Fe was used as a reference metal (Table SM4), although this may have led to an underestimation of EF because of anthropic input of Fe, especially in RD. Alternatively, Cr was also utilized (Table SM5), given its main lithogenic origin in Turin (Ajmone Marsan et al., 2008; Bonifacio et al., 2010; Padoan et al., 2016). The results using the crustal composition as reference values always exhibited values higher than local soil composition, but with a strongly similar pattern. In addition, using Cr or Fe as reference metals yielded similar results, identifying Sb and Pb as the most enriched metals in soils. Sb and Pb were averagely enriched ($EFs = 6$ and 5 , respectively) against Fe and local soil, while Cu and Zn appeared only slightly enriched ($EF = 2$). Conversely, Mn, Cr and Ni had mean EF values of 1. Taken together, these findings imply that Cr could also be a suitable reference element in soils in areas of diffuse natural background.

In the RD samples, Sb was still the most enriched element, followed by Cd, Cu and Pb. Average Sb EF values at traffic sites were 55 and 13 against crust and local soil, respectively. Additionally, Cr, Ni, and Zn were slightly enriched in RD with respect to the crustal composition, while Mn was not (EFs of 7, 9, 6 and 1, respectively).

From the EF results, an increasing gradient trend towards the city center was apparent (from A1 to A4), with higher values for almost all metals at the most trafficked sites (A1, A2 and S1).

3.5 Metal concentrations in size fractions

PSD of metals in soils and RD is a key parameter when performing an assessment of health risks from ingestion and inhalation. For inhaled particles, the most hazardous thresholds are at 10 and $2.5 \mu m$. For accidental ingestion, based on adhesion to the hands, the threshold was approximately $50-63 \mu m$, although certain studies have reported values up to $200 \mu m$ (Siciliano et al., 2009; Ruby and Lowney, 2012; U.S. EPA, 2011). This size was therefore selected for this study to be the maximum size for analysis.

Average *aqua regia* extractable contents of metals for each size fraction are available in Table 3.

In soils, all metals (except Cr and Ni) showed highest concentrations in the finest fractions. In particular, Fe and Mn had the highest concentrations in the $2.5-10 \mu m$ fraction, while Cu, Pb and Zn had the highest

concentrations with $<2.5\ \mu\text{m}$. To better interpret the data, as for bulk concentrations, Pearson correlations between metals for each size fraction were calculated. In the $<2.5\ \mu\text{m}$ fraction, Pb and Zn were highly related ($r = 0.90$; Table SM6 in the Supplementary Material) and could have originated from the same sources, like combustion or industrial processes. Zn could also derive from the same wear process as Cu (wheels and tires) - they are highly correlated in roadside soils ($r = 0.78$). Ni and Cr did not demonstrate any significant differences between different size fractions, with the latter being slightly enriched in the coarser fraction. This confirmed their mostly geogenic origin, as previously observed by Ajmone-Marsan et al. (2008).

In RD samples, Zn was of the highest concentration in the $<2.5\ \mu\text{m}$ fraction, almost four times the concentration in bulk samples, while the $2.5\text{-}10\ \mu\text{m}$ fraction was slightly less enriched. Industrial processes, such as smelting activities, emit Zn in the fine-size range, while Zn-containing tire wear particles have a peak between 2.5 and $10\ \mu\text{m}$ (Harrison et al., 2012). Cu, Sb and Pb had the highest values in $2.5\text{-}10\ \mu\text{m}$ particles, just as in the soil samples. This is congruent with the suggested source process (abrasion and wear of brakes and wheel clips) - brake emission tests show particle emission modes between 1.0 and $6.0\ \mu\text{m}$ (Grigoratos and Martini, 2015). Mn and Fe revealed little enrichment in the $2.5\text{-}10\ \mu\text{m}$ and coarser fractions, while Cr was greatest with respect to concentration in the bulk sample, as in the soils.

These results overall validate the importance, for RD samples, of discriminating between $<2.5\ \mu\text{m}$ and $2.5\text{-}10\ \mu\text{m}$ particles, as combustion processes mostly consist of particles $<2.5\ \mu\text{m}$, while wear processes produce coarser ($2.5\text{-}10\ \mu\text{m}$ and larger) particles.

In Table 4a, Pearson correlations in the $2.5\text{-}10\ \mu\text{m}$ size fraction of RD are reported, and results for $<2.5\ \mu\text{m}$ fractions are found in Table SM7. Confirming our hypothesis, Zn seemed to be correlated with Cu, Pb and Fe in particles of $2.5\text{-}10\ \mu\text{m}$, while they were not correlated to any other metal in particles $<2.5\ \mu\text{m}$, suggesting different sources in various size ranges. In the $2.5\text{-}10\ \mu\text{m}$ fraction, a significant correlation between C, Fe, Cu and Sb suggested, for C and Fe, an emission from brake wear, which is in agreement with their abundant presence in brake materials (Grigoratos and Martini, 2015). In the coarser fraction ($10\text{-}200\ \mu\text{m}$), no such relationship was observed. Cr and Ni are correlated between them and Ni with carbon and nitrogen, which was in line with a dominant natural origin.

No significant seasonal variability was found in soil samples nor RD samples, while the spatial variability of size-fractionated metals followed the same patterns observed in bulk samples. When calculating average concentrations in traffic and background sites, in soil samples, only Pb and Zn in the $<2.5\ \mu\text{m}$ fraction showed statistically significant variations between traffic and background samples. Instead, in RD, Cu, Pb, Zn and Sb were present in significantly higher concentrations at traffic sites for all size fractions.

Eventually, a comparison of elemental concentrations in braking and in acceleration sites (9+9 samples) was conducted. Within braking zones, Zn and Cu concentrations were higher than at acceleration sites in the $2.5\text{-}10\ \mu\text{m}$ fraction, although not significantly. This could possibly indicate that particles emanating from braking did not fall immediately on the road but were released also during the acceleration event, as recently found by Hagino et al. (2016).

In Table 4b, correlations considering only braking sites are reported. Here, contrary to the results, when all sites were pooled, Cr was significantly related to Cu, and Ni to Sb. Despite the limited number of samples, this could mean that a limited emission from brakes or road wear was also relevant for these metals, this process hindered by natural contributions when considering all sites.

The Cu:Sb ratio has been suggested in the literature to be a useful chemical tracer for brake wear particles. In our results, a shift between fine and coarse particles of RD was evident, being 12, 13, 26 and 36 being the ratios for $<2.5\ \mu\text{m}$, $2.5\text{-}10\ \mu\text{m}$, $10\text{-}200\ \mu\text{m}$ fractions and bulk RD, respectively. These values fall within the range found for RD particles $<10\ \mu\text{m}$, specifically from 7 to 17 (Amato et al., 2011; Grigoratos and Martini, 2015), while coarser particles are less enriched with Sb. The soil particles showed a larger and more constant ratio, between 16 and 24 for all fractions, indicative of a much lower enrichment of Sb in roadside soils. The

homogeneity of values could be based on the natural processes occurring in soils that change the size of the metal-bearing particles (Ajmone-Marsan et al., 2007) or on anthropic historical disturbances.

3.6 Bioaccessibility of metals

The bioaccessibility results showed the amount of a contaminant soluble in the gastrointestinal environment and, consequently, that would be available for absorption (Paustenbach, 2000). Average concentrations and percentages of the *aqua regia* extractable content for Cu, Ni, Pb, Sb and Zn at every site are listed in Table 5. Values for Fe and Mn are reported in Table SM8 (Supplementary Material), while values for Cr and Cd were below the detection limit (DL) in all samples, and, thus, not described herein.

In bulk soil samples, Pb was the most accessible metal, followed by Zn, Cu, Mn, Ni, Sb, Fe and Cr. Pb, Zn, and Cu were found in greater than 40% of the *aqua regia* extractable content, implying a significant risk in the case of ingestion. Cr and Fe were the least bioaccessible metals, in line with their inferred origin, with the first being <DL in most of the samples and Fe having an average bioaccessible fraction of 1% in soils.

In RD samples, Zn was the only element more bioaccessible than in the soils, followed by Pb > Cu > Mn > Sb > Fe > Ni > Cr. As in soils, metals enriched in the fine-size range were more bioaccessible, while Fe, Ni and Cr were the least bioaccessible metals. Sb had similarly low values in both matrices, aligned with its unique origin. These values are similar to the few studies that used the same methodology on RD samples, evidencing, probably, similar sources and chemical forms (Hu et al., 2011; Luo et al., 2011; Patinha et al., 2015).

As not all chemical forms were equally extracted, correlations between total and bioaccessible content could help in distinguish sources. For Pb, in particular (Tables SM2 and SM3 in the Supplementary Material), the two amounts were perfectly correlated in soils (Pearson $r = 0.98$) and well correlated in RD samples ($r = 0.82$). As at the less trafficked sites, Pb could be considered arising primarily from soil (Paragraph 3.1), and so we calculated correlations for RD samples in the highly trafficked sites ($n = 15$), trying to determine whether traffic was still a source of Pb. Here, total and bioaccessible Pb were less related in bulk samples ($r = 0.63$) than in size fractions, as they were perfectly correlated in all three fractions ($r > 0.95$). This could indicate that, at highly trafficked sites, different sources of bioaccessible Pb coexist; coarse Pb, probably deriving from soils, and fine Pb, most likely from traffic sources (e.g., brake pads, wheel clips, yellow paint).

No significant variations in bioaccessibility content with seasons were found with either matrix, probably also based on the limited number of samples.

Spatial distribution of bioaccessible metals in soils followed the trend seen for the total content, with Cu, Pb and Zn showing significantly higher concentrations at traffic rather than background sites. Traffic sites also a higher proportion of bioaccessibility, implying that, for these metals, traffic sources were more bioaccessible than those that were natural.

In RD samples, Fe, Cu, Pb, Sb and Zn were found at significantly higher concentrations (mg/kg) at traffic sites, but only Fe and Cu were observed in significantly greater proportions. This is probably because, contrary to Pb, Sb and Zn, at background sites, they mainly derive from geogenic, and less bioaccessible, sources (as suggested earlier). Fe, in particular, was considerably higher in concentration and proportion at trafficked industrial sites (A1 and A2) (10% and 7%, while the average was 2%) than all others. Ni and Mn did not exhibit any differences between traffic and background sites.

3.7 Bioaccessibility in size fractions

The average proportions for all metals and size fractions are outlined in Figure 3.

In soil samples Fe, Mn, Cr and Ni adhered to the same trend, with concentrations and proportion decreasing with the increase in size. Fine particles were significantly more bioaccessible at traffic than at background sites, consistent with the idea of a lithogenic origin of larger particles and a more anthropic, and bioaccessible, input for fine particles for all metals.

Cu, Pb and Zn had the most bioaccessible content and were found in the greatest proportions, with Pb being the most extractable metal. Along with Sb, they did not feature significant differences between size fractions, but they did significantly higher values at traffic sites. This is probably based on the long-term build-up of contamination, as in the case of Pb, and because in soils, metal-bearing particles can be aggregated by iron oxides, organic matter and carbonates or perturbed by the addition of fine particles and the mixing of roadside soils (Ajmone-Marsan et al., 2008).

In RD samples, the bioaccessible percentage of the finer fractions was higher than in soils for all metals, and a clear difference in bioaccessibility between fine and coarse fractions could be observed. This confirmed the probable different sources of metals in fine and coarse RD and, for a number of them, can probably pose a serious health risk. In particular, Pb, Zn and Cu were almost totally bioaccessible in the $<2.5\ \mu\text{m}$ fraction (98%, 96%, 89%, respectively) and in the 2.5-10 μm fraction (89%, 67% and 59%, respectively), while only 30% of Ni and Sb was extractable. As a result, bioaccessible Zn and Pb concentrations reached, in several samples, 1981 mg/kg and 612 mg/kg, respectively, in the 2.5-10 μm fraction and 1252 and 210 mg/kg in the $<2.5\ \mu\text{m}$ fraction. With the bioaccessible concentrations, average values were still higher than the legislative limit for the total concentration in soils (666 mg/kg for Zn and 245 mg/kg for Pb in the 2.5-10 μm fraction and 530 mg/kg and 139 mg/kg in the $<2.5\ \mu\text{m}$ fraction).

On the contrary, Fe, Mn, Ni and Cr followed the same trend observed in soils - the finer the fraction, the more bioaccessible the metals, though concentrations were twice that found in soils. No seasonal variability was observed in either matrix.

3.8 Statistical analysis

Chemometric data treatment was applied to the two data sets (RD and soil samples) separately and as a whole. Missing values were interpolated using the two values obtained in the other seasons, while for below the DL, a value of DL/2 was applied. Cd and bioaccessible Cr were discarded because of the high number of values $<DL$ and data sets were normalized and autoscaled utilizing z-scores.

Q-mode HCA was performed on the data sets to highlight similarities between variables, which could indicate common sources. The results were very similar for both media (RD and soils), thus only RD results were reported in Figure 4.

Metals appeared separated into four clusters. The first links together Cr, Ni, Mn and Fe, having the same main source in the parent material of soil and asphalt. The second cluster links C and N, as the organic fraction of RD could derive from either soil or anthropic activities, while the third was formed only by Pb and the extractable portion of Ni. These probably have a similar industrial source or mixed source as they can arise from traffic sources and soil. The last group is made up of all the metals with their primary origins in vehicular traffic, confirming the probable anthropic source of the extractable parts of Fe and Mn, while non-extractable Fe and Mn are soil-related, enclosed in a crystalline (or more stable) matrix.

4. Conclusions

Pseudototal and bioaccessible fractions of Fe, Mn, Cd, Cr, Cu, Ni, Pb, Sb and Zn were determined in RD and roadside soils of Turin. In the soils, the observed values were higher than reported in previous studies and above the legislative limits. Fine particles (<2.5 and 2.5-10 μm in size) were enriched for all metal (loids) except Cr and Ni, compared to the bulk samples, and spatial variation along the transect was more pronounced for elements mostly emitted by traffic sources (Cu, Sb, Pb and Zn).

In RD samples, the analysis of fractions identified two different sources for Zn (likely industrial in $<2.5\ \mu\text{m}$ fraction and tire wear in the 2.5-10 μm). The fraction between 2.5 and 10 μm was the most enriched for all metals but Zn, and almost all analyzed metals (except Mn) seemed to be highly correlated in this fraction. This

is probably because the particle emissions from brake, road and tire wear fall mostly within this dimensional range.

In the soil samples, the bioaccessibility of Fe, Mn, Cr and Ni increased in fine particles, likely based on the higher anthropic contribution and greater reactivity, while Cu, Pb, Sb and Zn had almost constant bioaccessibility for all sizes.

In the RD samples, the bioaccessibility of fine particles was clearly greater than in soils for all metals in the order $Pb > Zn > Cu > Ni \gg Cr$. For Pb, Cu and Zn, the bioaccessible fraction reached 90% in the $<2.5 \mu m$ fraction, which also had the most enrichment when compared to the earth's crust, so these results appear to be critical for the estimation of risk to human health in urban areas.

In general terms, the contents of the bulk samples should not be considered as reliable indicators of the concentration and bioaccessibility of metals in fine fractions of RD and soils, thus size fractionation appears to be a necessity to obtain more useful information for risk assessment in the urban environment.

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Table 1. Descriptive statistics for some soil and road dust properties (n=29 for RD and N=18 for soils).

	pH	TC	TN	Carbonates	Particle size distribution (mass %)				
		%	%	%	< 2.5 µm	2.5-10 µm	10-50 µm	50-200 µm	0.2-2 mm
Soil									
Mean	7.64	4.27	0.30	3.1	8	6	16	37	33
Median	7.68	4.20	0.27	2.4	5	6	14	34	35
Min	7.06	1.98	0.10	0.0	2	0.5	9	18	8
Max	8.13	7.94	0.63	9.5	16	17	30	71	60
Std. Dev.	0.34	1.53	0.13	2.6	5	4	6	13	16
Road Dust									
Mean	7.59	4.10	0.10	5.4	4	2	5	27	62
Median	7.59	3.65	0.10	3.8	2	2	3	27	60
Min	6.56	2.19	0.02	2.1	0.6	0.2	0	0	20
Max	9.76	8.77	0.32	16	24	8	17	62	98
Std. Dev.	0.70	1.69	0.07	3.8	5	2	4	17	19

Table 2. Descriptive statistics of metal pseudo-total content in soils (n=18) and road dust (n=29). All values are in mg/kg.

	Fe	Mn	Cd	Cu	Cr	Ni	Sb	Pb	Zn
Soil									
Mean	27513	857	0.6	128	405	254	5.4	319	286
Median	26039	817	0.5	100	332	229	4.9	133	242
Min	14523	589	0.2	26	147	145	1.5	38	96
Max	54955	1195	1.9	433	1048	465	13	1213	618
Std. Dev.	11742	173	0.4	97	269	93	3.2	331	141
Previous study^a	na	na	na	90	191	209	na	149	183
Legislative Limit	--	--	2	120	150	120	10	100	150
Road Dust									
Mean	24060	527	0.8	181	519	294	7.7	74	200
Median	23118	517	1	158	463	246	4	55	170
Min	9778	380	0.2	17	299	161	0.4	16	51
Max	43141	681	1.7	717	1248	678	33	189	827
Std. Dev.	9102	87	0.4	161	213	136	8.2	49	161

^a Biasioli et al., 2006

Table 3. Average concentration (mg/kg) of metals in size fractions, in traffic (TR) and in background (UB) sites.

Fraction	Site type	Fe	Mn	Cu	Cd	Cr	Ni	Pb	Sb	Zn
Road Dust										
< 2.5 µm	TR	15411	343	196	2	161	148	169	17	942
	UB	16166	400	129	1	149	148	113	10	414
2.5 - 10 µm	TR	32323	649	333	2	373	296	233	29	819
	UB	27242	883	101	2	353	348	99	9	337
10 - 200 µm	TR	31327	487	180	1	312	225	131	8	309
	UB	24935	385	40	0	259	112	45	1	139
Bulk	TR	24594	520	204	1	517	283	81	9	240
	UB	20236	546	29	1	502	329	33	1	68

Soil										
< 2.5 μm	TR	42934	1049	287	2	168	299	952	16	805
	UB	29356	1176	120	1	136	227	168	2	443
2.5 - 10 μm	TR	46001	1179	240	2	228	303	757	17	681
	UB	57497	1277	91	1	109	238	146	1	540
10 - 200 μm	TR	30715	579	88	0	202	158	289	7	346
	UB	31267	648	41	1	156	126	75	1	131
Bulk	TR	28684	840	145	0	432	256	368	6	305
	UB	21656	941	42	1	273	249	76	2	195

Table 4. Pearson correlations between metals in the 2.5-10 μm fraction. in all sites (a) and in only braking sites (b). In bold significant correlations ($p < 0.05$), $n=28$ for Table 4a and $n=9$ for Table 4b.

a	C	N	Fe	Mn	Cd	Cr	Cu	Ni	Pb	Sb	Zn
C	1										
N	0.90	1									
Fe	0.64	0.35	1								
Mn	0.70	0.65	0.55	1							
Cd	-0.46	-0.39	0.03	0.32	1						
Cr	0.26	0.06	0.38	0.25	-0.15	1					
Cu	0.54	0.21	0.76	0.21	-0.22	0.46	1				
Ni	0.63	0.58	0.446	0.66	-0.07	0.76	0.27	1			
Pb	0.49	0.14	0.61	0.25	-0.24	0.24	0.67	0.25	1		
Sb	0.64	0.41	0.73	0.32	0.03	0.14	0.75	0.16	0.64	1	
Zn	0.25	-0.13	0.51	0.18	-0.09	0.08	0.50	0.12	0.80	0.72	1
b	C	N	Fe	Mn	Cd	Cr	Cu	Ni	Pb	Sb	Zn
C	1										
N	0.86	1									
Fe	0.85	0.47	1								
Mn	0.69	0.24	0.58	1							
Cd	-0.87	-0.65	0.05	0.72	1						
Cr	-0.12	-0.61	0.57	0.15	-0.17	1					
Cu	0.90	0.56	0.85	0.25	-0.34	0.79	1				
Ni	0.40	-0.12	0.83	0.52	0.10	0.91	0.84	1			
Pb	0.74	0.36	0.63	0.35	-0.27	0.30	0.63	0.46	1		
Sb	0.50	0.15	0.79	0.56	0.03	0.43	0.67	0.65	0.62	1	
Zn	0.68	0.33	0.71	0.48	-0.19	0.28	0.64	0.49	0.89	0.90	1

Table 5. Average metal bioaccessible concentrations (mg/kg) and percentage of the *aqua regia* extraction in each site.

Site	Cu		Ni		Pb		Sb		Zn	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
Road Dust										
A 1	110	29	7	3	55	52	1.1	5	415	74
A 2	61	12	14	3	78	44	0.1	5	128	42
A 3	17	17	2	1	2	8	0.1	4	76	46
A 4	8	15	0	0	11	27	0.1	5	30	33
S 1	67	28	1	1	16	19	0.5	3	121	63
S 2	57	33	5	2	34	36	0.4	6	156	70
BO	43	18	4	1	34	36	0.3	5	116	61
RI	27	33	24	4	16	24	0.1	3	54	44
AG	5	16	11	3	3	11	0.02	1	32	43
PE	10	11	3	1	7	21	0.1	9	23	39
Soil										
A 1	40	35	14	7	33	38	0.3	6	140	49
A 2	122	71	20	7	382	59	0.6	6	270	53
A 3	45	44	11	5	181	54	0.3	4	108	45
A 4	34	40	11	5	131	45	0.3	6	70	33
S 1	44	18	39	12	351	74	0.2	5	111	41
AG	6	22	20	7	9	21	0.1	4	32	21
PE	29	43	20	10	82	56	0.5	11	32	11

Figure 1. Sampling sites. In red (A1 to S2) samples on the main road, in blue (RI and BO) secondary road sites and in green (AG and PE) urban background sites (background image from Google Maps (online), Digital Globe, 2016).



Figure 2. Concentrations (mg/kg) and standard deviations of Fe, Mn, Cr, Ni, Cu, Sb, Pb and Zn in RD and soil samples (reported with site name preceded by S). Sites from A1 to S2 are on the main road, BO, RI sites are in secondary streets, AG and PE sites are urban backgrounds.

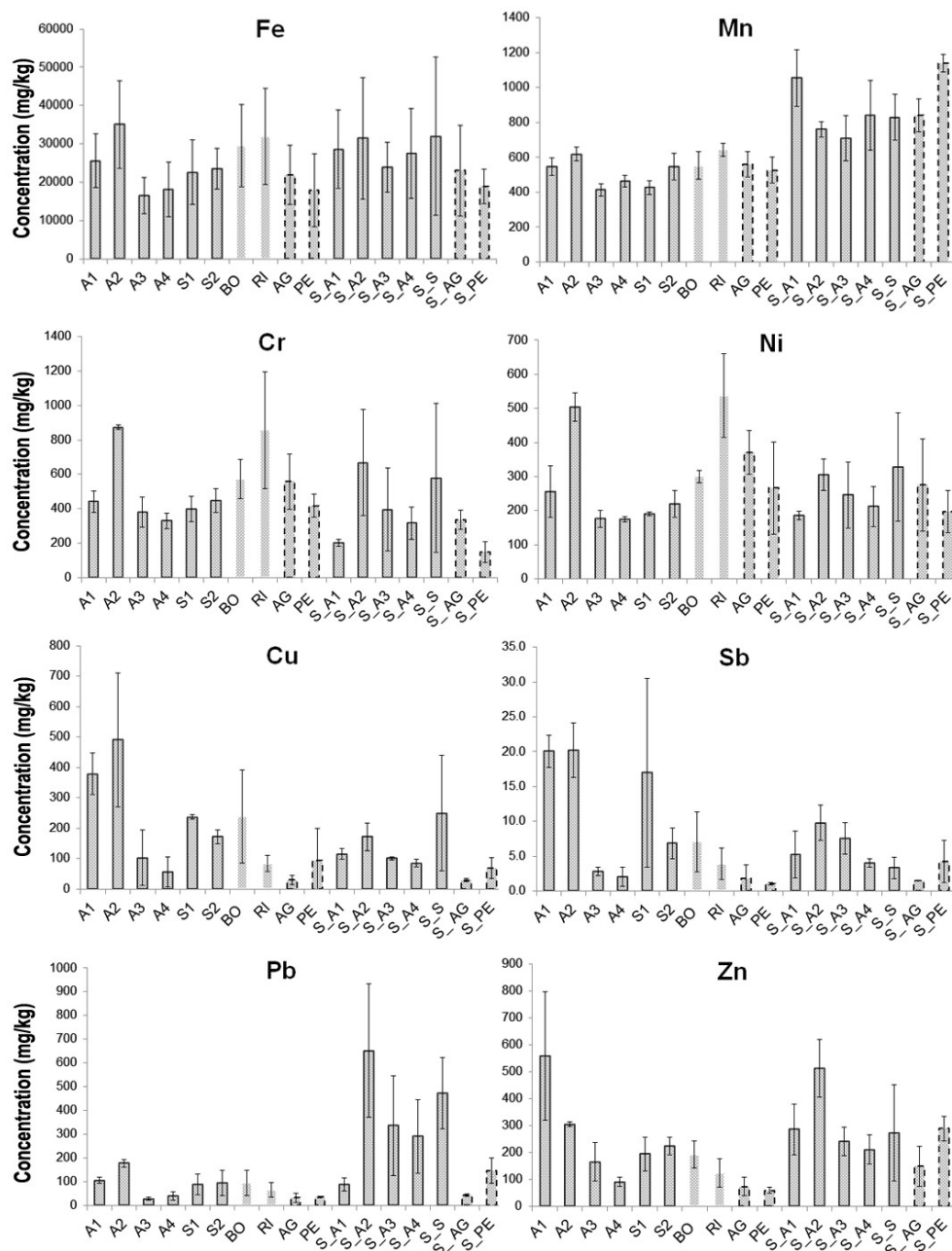


Figure 3. Bioaccessibility of metals in size fractions, percentage of bioaccessible to pseudo-total content.

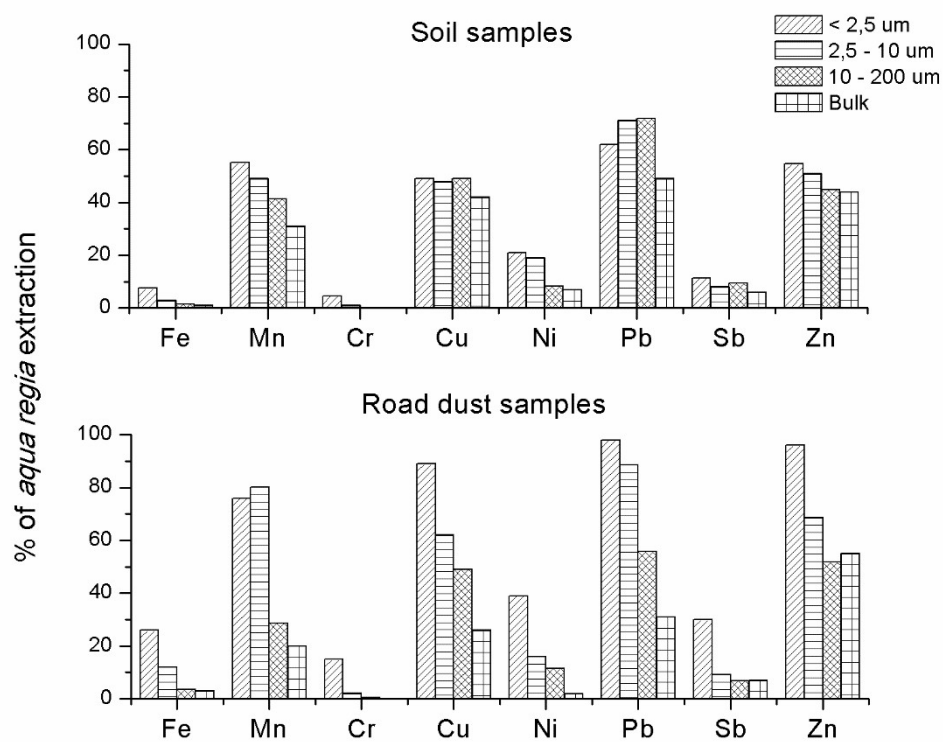


Figure 4. Dendrogram obtained by Q-mode HCA considering the data set of road dust samples.

